ISSUES AND THEORETICAL TOOLS TO GUIDE THE ACHIEVEMENT OF MOLECULAR CONTROL

Final Progress Report
under Army Research Office Grant No. DAAH04-95-1-184
for the Period of April 1, 1995 - January 31, 1998

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Statement of Problem Studied.

The research in this study addressed the problem of active coherent dynamical manipulation of molecular-scale events. The critical issues for exploration were (a) the degree to which control may be achieved, and (b) identification of the practical laboratory means for achieving control.

Summary of Results.

1. Competitive Tracking Of Molecular Objectives Described By Quantum Mechanics[1].

In this work, the control of molecular events by optical fields was sought with the methods of asymptotic inverse tracking, local track generation (model matching), and competitive tracking, which are extensions of exact inverse tracking. The methodology was applied to infrared dissociation of a diatomic molecules and selective dissociation of the stronger bond in a highly coupled linear triatomic system. The major appeal of these methods was that they did not require costly iterations, unlike other control studies in which optimization techniques are used, to design fields to achieve desired molecular objectives. It was found that in *exact* inverse tracking, where a requisite external field was obtained to exactly tract a prescribed objective expectation value as a function of time, a high degree of intuition was required to find an *a priori* objective track, such that the required fields were reasonable in terms of intensity and bandwidth. Furthermore, exact inverse tracking does not allow for tracking of multiple observables. The extensions of the inverse tracking method in this study helped to alleviate these drawbacks. In all of these extensions, the requisite field was computed locally in time, through minimization of a cost functional which contained terms designed to minimize the error between the objective and actual tracks and also minimize the field fluence. The objective tracks were described *a priori* as in exact inverse tracking, or from the evolving system state (local track generation). Competitive tracking allowed for the following of multiple observables, although none were tracked exactly. Locally generated tracks (model matching) required less physical intuition because it was easier to specify an objective track with current knowledge of the state of the system. However, the trade-off with this method was that prediction of the behavior of the tracked observables may be elusive.

2. **Optimal Control Of Optical Pulse Propagation In A Medium Of Three-Level Systems[2].**

This study resulted in developing an optimal control technique (OCT) in order to design a secondary optical pulse that could control the propagation of an arbitrary primary optical pulse in a medium consisting of three-level systems. The output primary pulse shape could be manipulated by designing the shape of the secondary pulse. The OCT was shown to be better than earlier proposed pulse schemes for protecting the magnitude and shape of the primary pulse from reshaping by the medium.

3. **Tracking Of Temporal Molecular Data: A Direct Inversion Algorithm For Recovering Potential Energy And Dipole Functions[3].**

This work presented a unified approach to inverting molecular potential energy and dipole functions from time-dependent measurements. The algorithm combined the regularized solution of a Fredholm integral equation of the first kind, containing data with time-dependent wavepacket propagation. The result was a nonlinear, noniterative algorithm to recover the potential and dipole functions from the time-dependent data. The recovered regions of these functions correspond to those sampled by evolving wavepackets associated with the laboratory data. Although the algorithm was designed to track temporal data, synthetic tracking data could be generated for inversion by the use of appropriate steady measurements.

4. **Unified Formulation For Control And Inversion Of Molecular Dynamics[4].**

In this work, we presented a unified approach for the control and inversion of molecular dynamics. The concept of molecular tracking tied the subjects to a common formulation. From molecular control, the time-dependent track of an observable operator was imposed *a priori*, and the control field was determined to meet the track. For extraction of the potential and/or dipole function, the time-dependent track was observed from laboratory data. A common three-step algorithm was presented to treat both seemingly unrelated problems.

5. **Determining Regular Orbits In The Presence Of Irregular Trajectories Using Optimal Control Theory[5].**

This work presented two general algorithms to determine regular orbits in the presence of irregular trajectories in a phase space of n degrees of freedom. The first algorithm searched for regular orbits with the energy of a free-floating parameter. The second algorithm sought regular orbits at constant energy. These two approaches utilized optimal control theory, to employ a small external control field that permitted a search among the irregular motion for the regular orbits. The optimizing algorithm naturally sought regular orbits with the control field turned off. Numerical results with a chaotic Hamiltonian showed the method to be effective in determining regular trajectories. If the system was completely chaotic in some region, the method determined which initial condition was the best one in order to achieve a nearly regular orbit.

6. Finding Regular Orbits[6].

This study resulted in a general method to determine regular orbits in the presence of irregular trajectories in phase space for a dynamical system of n degrees of freedom. A cost functional was introduced with a control field to guide the system towards regular orbits. Iteration of the optimizing algorithm naturally sought out regular orbits with the control field turned off. In the system was completely chaotic in some region, the method chose the best initial condition to achieve a nearly regular orbit. An illustration was presented for $n = 3$ and $n = 4$ dimensional dynamical systems.

7. Optimal Control Of Molecular Motion For δ-Target Probability Density[8].

This research presented a new δ-target approach to solving the problem of steering a molecular system to a desirable geometrical configuration, by an electromagnetic field. The δ-target technique was shown to provide good control, and the advantages of the δ-target approach were analyzed. In particular, in the weak field limit, the computational difficulties were considerably simplified; the control problem reduced to a task of propagating the δ-target wavefunction with the Hamiltonian of the molecular system independent of time. This simplification was of principal importance, as it permitted applications of optimal control theory to chemically interesting larger molecular systems.

8. δ-Target Optimal Control Of Molecular Dynamics: Application To A Rotating Diatomic Molecule[7].

The δ-target method proposed in an earlier study [*Chem. Phys. Lett.* **235**, 309 (1995)] was shown to significantly simplify the task of optimal control of molecular localization. In this research, we intended to study the application of the δ-target technique to a practically interesting case of a diatomic molecule, including rotation. Illustrative numerical examples were presented for the molecules NO and Na_2. The δ-target method was shown to provide good control when the rotational temperature was not too high. The optimal control solution was very robust and insensitive to small changes in the potential curves and transition dipole moment functions. It was shown that the field obtained within the linearized δ-target optimal control technique was considered for treating strong field nonlinear optimal control tasks. The computational advantages of the method was set out.

9. Adaptive Feedback Control Of Molecular Motion[9].

Control of molecular-scale event, including chemical reactions, has been a long sought-after goal. In this research, the central problem was to design control fields such that particular molecular objectives were achieved, while suppressing undesirable processes. The techniques of optimal control theory within quantum mechanics provided the framework for carrying out the designs. By replacing the model of the molecule in the computer with the actual molecule in the laboratory, various design problems were overcome. In this fashion, the molecule acted as an analog computer, solving its own dynamical equations in appropriate pump-probe experiments performed iteratively, and guided by a learning algorithm, to ultimately achieve the desired molecular control

objective. The practicality of this approach and some future directions of the field were also examined.

10. Optimal Control Of Population Transfer In An Optically Dense Medium[10].

In this research, we applied the optimal control technique (OCT) to design an optical pulse pair that controlled the population transfer in a medium of three-level atoms. The absorption and reshaping of the controlling pulses by the medium were taken into account. The efficiency of the population transfer was improved significantly, compared with designs that did not incorporate pulse absorption and reshaping.

11. Optimal Control Of Pulse Amplification Without Inversion[11].

This study applied an optimal control technique (OCT) to designing a secondary coupling pulse that could control the amplification of a given primary optical pulse in dense media of coherently prepared three-level λ-type atoms, without population inversion. Effects of pulse absorption, amplification, and reshaping by the medium, were incorporated in the OCT. We demonstrated numerically that shape-invariant, as well as shape-distorted, amplification without population inversion could be achieved by properly designing the shape of the coupling pulse. The maximum amplification obtainable was shown to be dependent on the initial atomic coherence, as well as the upper bound of the coupling pulse intensity. The group velocity of the primary pulse could also be controlled by the coupling pulse.

12. A Simplified Approach To Optimally Controlled Quantum Dynamics[12].

In this work, a new formalism for optimal control of quantum mechanical physical observables was presented. This approach was based on an analogous classical control technique reported previously [*J. Chem. Phys.* **102**, 226 (1995)}. Quantum Lagrange multiplier functions were used to preserve a chosen subset of the observable dynamics of interest. As a result, a correspondingly small set of Lagrange multipliers needed to be calculated, and they were only a function of time. This was a considerable simplification over traditional quantum optimal control theory [*Comp. Phys. Comm.* **63**, 71 (1991)]. The success of the new approach was based on taking advantage of the multiplicity of solutions to virtually any problem of quantum control to meet a physical objective. A family of such simplified formulations was introduced and numerically tested. Results for these new algorithms were compared with previously reported work on a model problem for selective unimolecular reaction induced by an external optical electric field.

13. Selective Excitation Of Molecular Eigenstates Using State-Dependent Optical Field Design[13].

This study proposed a new feedback algorithm for designing laser fields for state-selective excitation of molecular systems. The population amplitudes and relative phases of the eigenstates were used to generate a field which drove the population flow in the desired direction. Results were presented for both vibrational excitation of hydrogen fluoride and selective excitation of two degenerate electronic states in a model four-level system.

14. Optimal Control Of Piezophotonic And Magnetophotonic Switching In A Dense Medium Of Three-Level Atoms[14].

In this research, we applied optimal control techniques to maximizing the absorptionless index of refraction, the density-dependent piezophotonic switching between absorption and amplification, and the ground-state energy-level-spacing-dependent magnetophotonic switching of susceptibility, in a dense medium of coherently prepared three-level system.

15. On The Generality Of Optimal Control Theory For Laser-Induced Field Design[15].

There has been much discussion in the literature about the relationship between optimal control theory for manipulating molecules and more traditional perturbation theory techniques. In this work, we rigorously establish the relationship between these two approaches, and demonstrate that perturbation theory techniques are a special limiting case of optimal control theory.

16. Perturbative Formulation Of Optimal Control Approach For Two-Photon Transitions. Reduction To An Eigenvalue Problem[16].

This study introduced a perturbative formulation to reduce the task of designing optima controls of molecular motion. The method provided multiple optimal control fields as eigenvectors corresponding to the positive eigenvalues of a matrix $\{A_{mn}\}$. Analytical equations for the matrix elements A_{mn} were derived. Numerical examples were given for simple three- and four-state molecular systems. The method was shown to be computationally simple and efficient in providing good quality control results.

17. Induced Transient Birefringence Of A Resonantly Pumped Molecular Gas[17].

In this work, we presented a theoretical study of the induced transient birefringence of a low density homogeneous molecular gas in a resonant pump-probe experiment. The molecular coherent state induced by the resonant pump field was described the second-order perturbation theory. The induced birefringence could be detected by a delayed probe pulse propagating through the molecular medium after illumination by the pump pulse. In the case of a nonresonant probe, the birefringence was linearly proportional to the mean value of the electronic polarizability of the molecular gas. The birefringence signal was composed of distinct components, due to population change and those of rotational, vibrational, and mixed rotational-vibrational origins. This was demonstrated by numerical simulations on Li_2 gas. Moreover, the quantum beats contained in the birefringence, as a function of the time delay between the pump and probe pulses, were dominated by pure rotational motion. Finally, the birefringence was sensitive to the shape of the applied pump pulse, and dependent on the spectral phase of the pump pulse.

18. Feasibility Of Using Photophoresis To Create A Concentration Gradient Of Solvated Molecules[18].

The objective of this work was to estimate the feasibility of creating a measurable concentration gradient of molecules in a solvent by a laser-driven photophoresis process. The molecules were dissolved in a suitable solvent that was not significantly absorbing at the applied radiation frequency. The molecule was anisotropic, or ideally, propeller shaped, and was an appropriate transition dipole capable of driving rovibrational motion. The polarization of the laser was taken as rotating slowly with the molecules. The resulting torque-driven hindered rotation imparted a forward thrust, and thus created a net flow of the molecules which could set up a concentration gradient in a finite cell. The relevant physical parameters were estimated with the aid of instantaneous normal mode and molecular dynamics simulation methods on a prototype system, and the results indicated that a detectable concentration gradient could be established. A practical issue was to treat heating and resultant mixing or turbulence in the medium.. Laboratory experiments are needed to further explore the photophoresis process.

19. Upper And Lower Bounds On The Control Field And The Quality Of Achieved Optimally Controlled Quantum Molecular Motion[19].

A large class of problems in optimally control quantum or classical molecular dynamics was multiple solutions for the control field amplitude. A denumerably infinite number of solutions may exist, depending on the structure of the design cost functional. This was proved with the aid of perturbation theory, by considering the electric field as the perturbating agent. In carrying out this study, an eigenvalue (i.e., a spectral parameter) appeared, which gave the degree of deviation of the control objective from its desired value. In this study, we developed a scheme for constructing upper and lower bounds for the field amplitude and spectral parameter for each member of the denumerably infinite set of controls solutions. The bounds could be tightened if desired. The study was primarily restricted to the weak field regime, although the bounds for the strong field nonlinear case were also presented.

20. Learning Control Algorithm For Nonlinear Maps[20].

In this work, a feedback optimal control algorithm was developed for N-dimensional maps, which used learning-based optimal control techniques. The algorithm had two steps: (1) learn the control of a reference map containing a stochastic term, and (2) apply the learned control to the laboratory system employing real time feedback. The stochastic component of the learning step was important to provide a close knit family of controls, to handle laboratory uncertainty and noise. As an example, the formalism was applied to simulated two- and three-dimensional nonlinear laboratory maps in the presence of noise.

21. Control Of Classical Regime Molecular Objectives - Applications Of Tracking And Variations On The Theme[21}.

This research examined the applicability of variations of exact tracking, including asymptotic tracking, state-dependent trajectory tracking, and competitive tracking, for the

problem of generating feasible external laser fields for control of classically modelled molecular motion via external laser fields. Applications were considered to the selective unimolecular dissociation of the stronger bond of highly coupled linear triatomic molecules. Specifically, we explored two variations of exact tracking, namely, asymptotic energy tracking and competitive acceleration tracking. In the former case, we found that a high degree of physical intuition was needed to specify a desirable energy track *a priori*. In the latter case, less physical intuition was necessary, since we only needed to specify the desired accelerations for given displacements, momenta, and potential at each time, instead of following a prescribed track. However, a trade-off with this method arose, due to the difficulty in predicting the relevant observables such as the dissociation probability before actually integrating the equations of motions.

Publications Resulting from Support under this Grant.

1. Competitive tracking of molecular objectives described by quantum mechanics, Y. Chen, P. Gross, V. Ramakrishna, H. Rabitz, and K. Mease, *J. Chem. Phys.*, **102**, 8001-8010 (1995).

2. Optimal control of optical pulse propagation in a medium of three-level systems, N. Wang and H. Rabitz, *Phys. Rev. A*, **52**, R17-R20 (1995).

3. Tracking of temporal molecular data: A direct inversion algorithm for recovering potential energy and dipole functions, Z-M. Lu and H. Rabitz, *Phys. Rev. A*, **52**, 1961-1967 (1995).

4. Unified formulation for control and inversion of molecular dynamics, Z.-M. Lu and H. Rabitz, *J. Phys. Chem.*, **99**, 13731-13735 (1995).

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6. Finding Regular Orbits, J. Botina and H. Rabitz, *Phys. Rev. Lett.*, **75**, 2948-2951 (1995).

7. Optimal Control of Molecular Motion for δ-Target Probability Density, V. Dubov and H. Rabitz, *Chem. Phys. Lett.*, **235**, 309-315 (1995).

8. δ-Target Optimal Control of Molecular Dynamics: Application to a Rotating Diatomic Molecule, V. Dubov and H. Rabitz, *J. Chem. Phys.*, **103**, 8412-8423 (1995).

9. Adaptive Feedback Control of Molecular Motion, H. Rabitz, *NATO ASI Ser., Ser. C*, **470**, 181-193 (1995).

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11. Optimal control of pulse amplification without inversion, N. Wang and H. Rabitz, *Phys. Rev. A*, **53**, 1879-1885 (1996).

12. A simplified approach to optimally controlled quantum dynamics, J. Botina, H. Rabitz, and N. Rahman, *J. Chem. Phys.*, **104**, 4031-4040 (1996).

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20. Learning control algorithm for nonlinear maps, J. Botina and H. Rabitz, *Phys. Rev. E*, **56**, 3854-3858 (1997).

21. Control of Classical Regime Molecular Objectives - Applications of Tracking and Variations on the Theme, Y. Chen, P. Gross, V. Ramakrishna, H. Rabitz, K. Mease, and H. Singh, *Automatica*, **33**, 1617-1633 (1997).

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REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	2/2/99	Final Report; 4/1/95-1/31/98

4. TITLE AND SUBTITLE
Issues and Theoretical Tools to Guide the Achievement of Molecular Control

5. FUNDING NUMBERS
DAAH04-95-1-0184

6. AUTHOR(S)
Herschel Rabitz

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
Trustees of Princeton University
Office of Research and Project Administration
Princeton University
5 New South Building
Princeton, NJ 08544

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 33587.9-PH

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This research concerned the control of chemical and physical phenomena at the molecular scale. Theoretical design tools were employed, pulling together concepts from engineering, control, and quantum dynamics. The research explored the boundaries of achievable control over molecular-scale event, especially using external optical fields. These studies indicate that a broad spectrum of molecular-scale processes should be amenable to successful laboratory control. In addition, the foundations were established for using similar concepts to extract fundamental Hamiltonian information from associated ultrafast dynamics observations. It is concluded that, in general, various quantum learning control techniques would be most effective for both manipulating molecules and deducing information about their interactions.

14. SUBJECT TERMS	15. NUMBER IF PAGES
Quantum Mechanics, Control, Lasers	10
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL